Full Length Article

Functionalization of steel surfaces with organic acids: Influence on wetting and corrosion behavior

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ABSTRACT

Self-assembled monolayers (SAMs) have been used to tailor surface properties of different metal surfaces. Typically SAMs can be bound to surface hydroxyls of a thin oxide layer that forms on the surface of a less noble metal and dominates its properties. The effects of SAMs with different anchoring groups and chain lengths regarding wettability, corrosion resistance and homogeneity of the layer were studied in detail. Alkyl carbonic and phosphonic acids were selected to create a hydrophobic layer on the surface of stainless steel ASIS 316L and on carbon steel N80. SAMs were formed by dip-coating of the samples in an organic acid ethanolic solution. Sum frequency generation (SFG) analysis together with contact angle and electrochemical measurements were carried out to explore correlations between tailored wettability, corrosion resistance, and layer homogeneity on one side, and the chain length, anchor group, concentration and immersion time on the other side. The homogeneity of the layers as well as the resulting surface hydrophobicity increased with an increase of the immersion time, the contact angle reached a maximum (ca. 120°) for an immersion time of approximately 2 days.

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1. Introduction

Different techniques are used to enhance the properties of materials. Coatings and self-assembled monolayers (SAM) can be highly advantageous, to modify the surface performance but do not change the properties of the substrate [1–3]. Coatings can have functional or decorative uses [4]. In order to protect a material, the coating should cover the full surface of the substrate [5,6]. Different methods are used to apply coatings, among them are dip-coating [7], spin-coating [8], electroless [9–11] and electrodeposition [12,13], physical vapor deposition [14] and chemical vapor deposition [15,16]. Self-assembled monolayers are formed by a chemical interaction between the anchor group of organic molecules and the substrate surface which has often a thin oxide surface layer that is terminated by surface hydroxyl groups. Molecules forming self-assembled layers have an organic/inorganic chain and a head group determining the achieved surface properties [17–19].

Organic acids have been previously used to improve the corrosion resistance of different metals. For example it has been shown that phosphonates are able to act as corrosion inhibitors [20–23]. Other studies have shown a correlation between the head group and wetting behavior [18]. A surface has to fulfill two requirements in order to be considered superhydrophobic, a water contact angle (CA) over 150° and a sliding angle lower than 5°. This type of surfaces were discovered by the study of the lotus leaf [9,24–26]. In order to achieve a superhydrophobic surface two properties have to be reached, a low surface energy and a roughness in a micro/nano scale, both effects act sinergetically [27–30]. A low energy surface has a low wettability, coatings or self-assembled monolayers can be used to lower the wettability, the following tail groups are commonly used with decrease of energy in the order of $CH_2 > CH_3 > CF_2 > CF_2H > CF_3$ [29,31]. Recent studies show a stability of some alkylphosphonic acids on stainless steel where the chain length plays a role in the stability of the hydrophobic layer for different

Table 1
Nominal composition of SS 316L and CS N80 [36–38].

	C	Si	Mn	Ni	Cr	Mo	S	P	Fe
SS 316L	<0.03	<1	<2	10	18	3	<0.03	<0.045	Balance
CS N80	0.31	0.19	0.92	–	0.20	–	0.08	0.01	Balance

acidic/basic media as well as dry heating and physiological conditions [32].

Stainless steel 316L is used in several fields due to its high corrosion resistance and its biocompatibility with the human body [33]. Carbon steel N80 (Table 1) is frequently used for instance in oil industry for well construction, flow-lines and pipe-lines [34]. These two steels have a very different corrosion behavior as well as surface chemistry: in the case of 316L, a passive film strongly enriched of Cr-oxides is spontaneously formed on the surface under many conditions providing high corrosion resistance. Carbon steel, on the contrary, only shows passivity in alkaline solution [35]. Therefore, it is of interest on the one hand to study the formation of organic monolayers on the two steel surfaces with a different surface chemistry, and on the other hand the influence of these organic monolayers on corrosion protection of an actively and passively corroding material. These interactions have been studied in this present work by a combination of techniques probing the nature of the formed coatings (SFG, XPS, contact angle) and electrochemical characterization used to study the resulting corrosion protection properties of these layers.

2. Materials and methods

2.1. Sample preparation

Carbon steel N80 (CS N80) and stainless steel AISI 316L (SS 316L) were used as substrates (see Table 1 for nominal compositions of the materials). For both materials the samples were cut with dimensions of 20 mm × 20 mm × 5 mm. Afterwards, they were grounded with SiC paper from 80 to 4000 grades, and then polished with diamond powder of 6 and 1 µm. Due to the very low corrosion resistance of CS N80, a solution 3:1 ethanol-glycol instead of water was used during the grinding process to prevent corrosion during surface preparation. Finally, all samples were sonicated in ethanol for 2 min and dried with hot air.

Four solutions were used to create organic layers on the surface of the samples, namely stearic acid (octadecanoic acid) ethanolic solution of 1 mM, ODPA (octadecylphosphonic acid) ethanolic solution of 1 mM and myristic acid (tetradecanoic acid) ethanolic solution with two concentrations, 0.1 M and 1 mM. The immersion time was between 1 h and 8 days. Afterwards, the samples were removed from the solution, thoroughly rinsed with ethanol to remove non-bound residues, and dried with nitrogen.

2.2. Contact angle measurements

For the contact angle measurements, a Drop Shape Analyzer KRÜSS DSA30 was used. Five drops of distilled water of 3 µL volume were placed in the center of the sample, in order to avoid any border effects. Subsequently, an average value and the standard deviation of the contact angle were calculated. The contact angles were measured for samples treated with immersion times of 1 and 6 h, and 1, 2, 4, 6 and 8 days.

2.3. Sum-frequency generation (SFG) spectroscopy

SFG spectroscopy is based on the spatial and temporal overlap of two pulsed laser beams one in the infrared (IR) and one in the visible wavelength region (Vis) on the sample surface where a photon with the sum frequency of the two incident beams is generated in a three-wave mixing process. The SFG intensity can be described by nonresonant contributions due to nonresonant electronic transitions at the substrate surface and resonant contributions due to resonant excitations of molecular vibrations of surface adsorbates that are caused by the interaction with the IR pulse. The vibrational bands resulting from resonantly excited molecules can be described by Lorentzian curves. The amplitude of the bands depends on both the molecular number density and on the orientational average of the hyperpolarizabilities and thus the orientation distribution of surface adsorbed molecules. Accordingly, the SFG intensity depends on the coverage and the molecular order of surface molecules and is therefore well suited to study molecular monolayers. Further details on the theory and principles of SFG can be found in the literature [39].

SFG spectra presented here were recorded with our 1 kHz home-built broadband SFG spectrometer, which is described in detail elsewhere [40]. The visible beam had a pulse energy of 15 µJ at 800 nm and a FWHM (full-width half maximum) of $\leq$6 cm^{-1}, while the broadband IR beam had a FWHM bandwidth of >200 cm^{-1} at 3500 nm and pulse energies of 35 µJ. IR, Vis and SFG beams were all polarized parallel to the plane of incidence (ppp polarizations).

Because the lifetime and the dephasing time of molecular vibrations are typically in the range of a few ps and are thus much longer than the lifetime of the nonresonant electronic excitations (<0.1 ps), they can be efficiently suppressed by delaying a time-asymmetric visible pulse versus the femtosecond IR pulse [41,42]. For that reason, all spectra shown in this article were recorded at an IR-Vis time delay of 300 fs and thus with full suppression of the nonresonant contribution.

All measurements were performed with an acquisition time of 120 s. In order to correct for the frequency dependence of the IR intensity, SFG spectra were normalized to the nonresonant signal of an air-plasma cleaned polycrystalline Au film.

2.4. Surface analysis

For the composition analysis attenuated total reflection – infrared ATR-IR (Thermo Scientific Nicolet 6700/Smart iTR) was used. The wavenumber studied was in the range between 500–4000 cm^{-1} with diamond as special ATR-crystal. Stainless steel samples were immersed in the different organic acids solution for a period of 2 days.

In addition, the surfaces of samples were characterized by X-ray photoelectron spectroscopy (XPS) (Phi-5600) using Al K α radiation, measuring the atomic concentration of different elements on a modified surface. Depth profiling was performed by sputtering with Ar at 3.5 kV, corresponding to 39 nm/min SiO$_2$.

2.5. Electrochemical measurements

To characterize the corrosion behavior, potentiodynamic polarization curves were measured with a Zahner Elektrik GmbH setup using a three electrode system. The samples were used as a working electrode and were introduced in a cell with an O-ring sealed opening exposing to the electrolyte a circular area with a diameter of 1 cm 80 mL of 0.1 M H$_2$SO$_4$ solution was used as an electrolyte. For further studies a second electrolyte of H$_2$SO$_4$ with a pH of 4 was also used. The counter electrode was platinum and the reference electrode was Ag/AgCl in a 3 M KCl solution which has a shift of +0.210 V compared with a standard hydrogen electrode (SHE). Three samples for each coating were prepared for potentiodynamic polarization measurements; afterwards the one with the intermediate values among the three be presented. The polarization scan was between −0.750 V and 1.5 V for the carbon steel samples and between −0.55 V and 1.5 V for the stainless steel samples,